

MON/01/OCT/2007 13:05

FAX Nr.: 069-7165-2331

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September 29, 2003

Dated: September 29, 2003

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P-002
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OCT 04 2007

Docket No.: NY-CHEM-MT-206.1-
Cont.-US

(PATENT)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of:
Klaus-Dieter NITTEL, et al.

Application No.: 10/830,181

Group Art Unit: 1742

Filed: April 22, 2004

Examiner: Zheng, Lois L.

For: **METHOD FOR APPLYING MANGANESE
PHOSPHATE LAYERS**

Commissioner for Patents
P. O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

DECLARATION UNDER RULE 132

Sir:

1. I am Ralf Schneider, a materials' science investigator employed by the assignee of the present invention. I have three (3) years education in materials' science development and testing and attended five (5) years of evening school in mechanical engineering. I have been employed by Chemetall GmbH since 1995 and I have been working in the field of manganese phosphating since then.
2. I am familiar with the patent application, and I am familiar with the Office Action dated April 4, 2007.
3. I submit this declaration with the accompanying data in view of the Examiner's analysis of the application, particularly the Examiner's 35 U.S.C. § 103(a) rejections of claims 8-16.

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4. I have reviewed all of the cited references including Hansen et al., US 3,860,455, and I have especially reviewed Example 1 with the bath of Experiment C of Hansen et al., which relates to a manganese phosphating without nitroguanidine for the coating of steel. In my experiments, I used the process succession of column 4, lines 14 to 22 of Hansen et al.. In Table 1 of Hansen et al., first the fresh starting bath, then beginning in the second line of the last page of this table the makeup composition for the replenishment of the bath, further on the bath composition after throughput of 2 m² steel surface (probably 50 steel sheets) and finally data of the coating weight of the phosphate coating, sludge weight and chemical consumption are mentioned. No nitroguanidine was added, nor was the possibility of adding nitroguanidine disclosed in Hansen et al..

5. The following four experiments were conducted by me on the basis of this Experiment C of Hansen et al.:

Variant a) with a fresh solution without nitroguanidine and without addition of Fe²⁺.

Variant b) with a fresh solution with 1 g/L of nitroguanidine and without addition of Fe²⁺.

Variant c) with a fresh solution with 1 g/L of nitroguanidine and with addition of 1 g/L of Fe²⁺.

Variant d) with a fresh solution with 6 g/L of nitroguanidine and without addition of Fe²⁺.

Three steel sheets each were coated for a variant.

The following formulations were used and the data from the experiments are set forth below in Table 1.

Table 1:

Content in g/L; Variant	a)	b)	c)	d)
Mn	12.1	12.1	12.1	12.1
Fe ²⁺	-	-	1	-
P ₂ O ₅	36.9	36.9	36.9	36.9
NO ₃	3.9	3.9	3.9	3.9

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Ni	0.34	0.34	0.34	0.34
Nitroguanidine	-	1	1	6
Free Acid FA	15.5	15.5	15.5	15.5
Total Acid TA	82	82	83	82
S Value = FA : TA _{Fischer}	0.30	0.30	0.30	0.29
Total P ₂ O ₅ = Phosphate	66.5	66.5	66.5	66.4
SV = TA : FA	5.3	5.3	5.4	5.5
pH	2.4	2.4	2.4	2.4
Temperature °C	92	92	92	92
Pickling Rate g/m ²	12 - 13.*	12 *	8 *	12 *
Gasing Time min	4	2	2	2
Coating Time min	10	10	10	10
Coating Weight g/m ²	12.7	15.4	10.9	12.8
Pickling Rate to Coating Weight	0.98 *	0.78 *	0.73 *	0.86 *
Typical Crystal Sizes µm	1 - 10	2 - 10	2 - 8	2 - 8
Average Crystal Size µm	about 4	about 5.5	about 5	about 5
Roughness R _a µm	7.6	8.3	6.4	9.0

* estimated

The point number in Table 1 of Hansen et al. is the total acid TA. The S value is calculated as the ratio of free acid FA to total acid TA.

It was found that after three steel sheets were coated, there the pickling effect was such that about 0.4 g/L of Fe²⁺ including a small amount of Fe³⁺ were taken up into the bath.

The crystal sizes were estimated from scanning electron microscope photographs (enclosure I).

6. The following tendencies could be observed:

A) The gasing time, which indicates the pickling time of the acidic solution on the metallic surface by the generation of hydrogen gas, is significantly reduced by the addition of nitroguanidine, which means that there is a significantly shorter coating time.

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B) The pickling rate is lowered as the gasing time is shortened by the content of nitroguanidine, but is especially improved by the combination of contents of nitroguanidine and Fe^{2+} . The pickling effect in a process according to the present application was significantly reduced compared with a manganese phosphating process without nitroguanidine addition, apparently because of the passivation effect of nitroguanidine. Less pickling is favorable because of shorter treatment time, less consumption of chemicals and less reaction products. Further more, because of the generation of hydrogen gas during the pickling, a lowered hydrogen gas emission is favorable because of lower risk of the hydrogen brittling of the steel.

C) The coating weight and, therefore, the thickness of the coating are significantly reduced if there is a certain content of nitroguanidine and Fe^{2+} . This probably also indicates a lowered consumption of chemicals for the process of the invention, which is favorable.

D) The crystal sizes of the coating are within acceptable limits.

E) The roughness R_a of the surface of the phosphate coating which was measured with a roughness measurement device Perthometer S8P for a measured line of 250 μm is lowered for the process of the invention. The lower the roughness R_a is, the lower is the abrasion, which is favorable.

F) Therefore, as the roughness R_a of the surface of the phosphate coating is lowered, the sliding friction should be significantly reduced too, which is very important for the practical application of manganese phosphated articles.

G) Further on, the noise generation during the continuous use of sliding objects like manganese phosphated gear components is significantly lowered if their roughness is lowered.

7. According to my experience and knowledge in the art, a bath showing no nitroguanidine addition (like variant a)) would show after such a throughput experiment a significantly higher Fe^{2+} content and the time to use such iron rich bath is significantly reduced as the bath has to be chemically modified to extract the iron content by oxidation and precipitation, when the content of Fe^{2+} is at about 50 % of the content of Mn. This time is significantly shorter than for the further variants b) to d), which could be used for a longer time. The bath without nitroguanidine

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content will have a stronger decrease of the ratio of TA : FA which increases an earlier pickling effect as in the baths of the other variants b) to d). The resulting phosphate coatings would typically be a bit coarser than the phosphate coatings of the other variants b) to d). Such coating would typically have a relatively high Fe content and would be less adequate for a use in sliding friction.

8. According to my experience and knowledge in the art, a bath showing a nitroguanidine addition according to the present patent application (like variant b)) would show, after such throughput experiment, a longer stability, would have a less strong decrease of the ratio of TA : FA which increases later the pickling effect as in the bath of variant a) and would result in finer crystalline coatings than in variant a). Note that after having pickled only one steel sheet, there is a content of Fe^{2+} in the bath of about 0.1 g/L which already generates a clearly positive influence on the coating of the second and third steel sheet. A content of Fe^{2+} in the bath of 1 g/L in a laboratory scale would be probably reached after coating of e.g. about 4 to 12 steel sheets, depending strongly on the bath volume. The resulting phosphate coatings would clearly have the best properties for sliding friction, but probably even too the best results for corrosion protection and other properties. Typically, they would have the smallest crystal sizes and best generation and performance of the coatings.

9. According to my experience and knowledge in the art, a bath showing a very high nitroguanidine addition like 6 g/L (like variant d)) would show after such throughput experiment the reaction products in the bath, would show disadvantages in the forming of the phosphate coatings and may even lead to the problem of no longer forming closed coatings.

10. In the above mentioned Office Action, the claims 8 – 10 and 13 are rejected as being unpatentable over Hansen et al. (US 3,860,455) in view of Clifford et al. (US 2,375,468).

Hansen et al. teaches phosphatings without the use of nitroguanidine.

Clifford et al. teaches the use of nitroguanidine for phosphatings with manganese phosphate, zinc dihydrogen phosphate and manganese dihydrogen phosphate (examples 1 – 3). The type and quality of these phosphatings were already evaluated in a first Declaration. Now I have

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performed nearly identical experiments for example 1 and made scanning electron microscope photographs.

11. These photographs (enclosure II) show the following:

- 1.) 60 min room temperature coating without nitroguanidine: No visible coating, coating weight practically zero, metallic material removed by pickling (pickling rate) of about 1.6 g/m².
- 2.) 10 min 80 °C coating without nitroguanidine: No closed coating which is necessary for corrosion resistance or for coldforming, coating weight of about 1.6 g/m², pickling rate of about 19.9 g/m².
- 3.) 60 min room temperature coating with about 3 g/L of nitroguanidine: No visible coating, coating weight practically zero, pickling rate of about 17.8 g/m².
- 4.) 10 min 80 °C coating with about 3 g/L of nitroguanidine: Non-closed, extremely inhomogeneous coating with singular huge crystals, coating weight of about 19 g/m², pickling rate of about 17.5 g/m².

All these photographs reveal the metallic surface, but do not show a phosphate coating. Only the photograph 4.) shows a beginning phosphate coating with areas of the metallic surface and some huge and much too big phosphate crystals.

The results are so extremely poor that one of skill in the art of phosphate coatings would not believe in any difference and tendency of the experiments of Clifford et al.. An expert in the art cannot visualize an advantage from adding nitroguanidine from these data and photographs.

12. It is my understanding that Hansen et al. cannot be successfully combined with Clifford et al. or other references to arrive at the claimed invention.

13. I believe that the effects of nitroguanidine in comparison to other phosphating accelerators are very different as nitroguanidine does not have an oxidizing effect and clearly works in a very different manner in comparison to other accelerators as disclosed, e.g., in Hansen et al..

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14. Hansen et al. discloses a content of Fe^{2+} in the range from 0 to 30 g/L (col. 2, l. 11), but does not teach how this content could be limited in a phosphating bath, which is used for coating of a huge amount of steel surfaces, of which a lot of Fe^{2+} is pickled out. The phosphating system of Hansen et al. would not limit the content of Fe^{2+} . I believe that the bath would finally show a content of Fe^{2+} in the range of about 5 to 9 g/L although it describes the possible use of strongly oxidizing accelerators, which content is quite too high, as there will typically not be an adequate formation of a phosphate coating according to my experience. The bath would have to be regenerated earlier by a separate oxidizing step to decrease the iron content by sludge formation, which is a time-consuming process step which significantly interrupts the process for coating of metallic articles.

15. The content of Fe^{2+} according to the present application is limited by a shortened pickling time and therefore by a reduced amount of ions pickled out of the metallic surfaces.

16. Hansen et al. and Clifford et al. do not indicate any crystal sizes, any roughness information, any corrosion resistance, any paint adhesion or any sliding friction quality.

17. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Respectfully submitted,

By Rolf Bier

Date 1-10-2007

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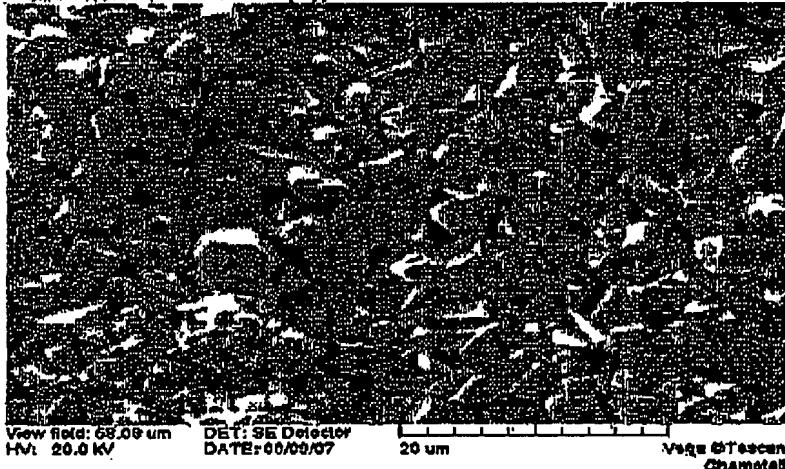
P. 009

Enclosure I

6120419; GBG4098; CN4;
Patent 3.860.455

09.08.2007
SCDE

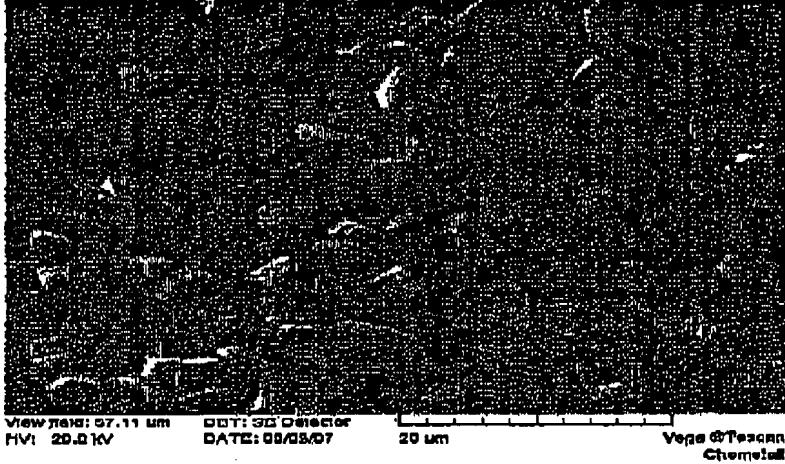
Varilnate A: Ohne Fe(II), ohne CN4



SG: 12,7 g/m²;

X=2000

Variant C: 1 g/l Fe++; 1 g/l CN4



SG: 10,9 g/m²;

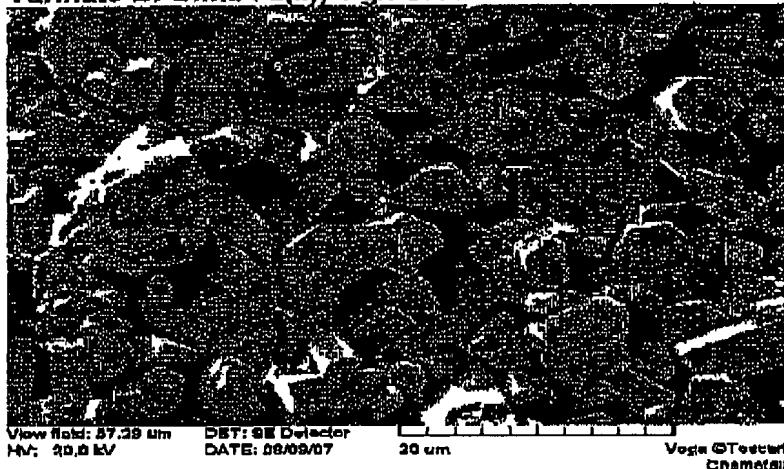
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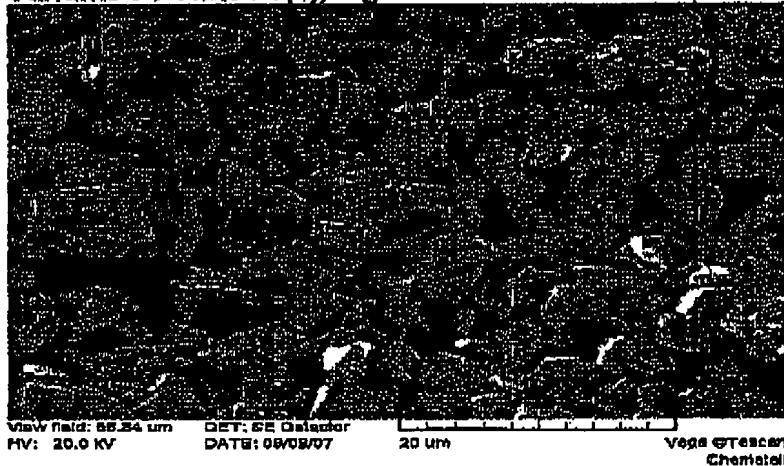
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Varinate B: Ohne Fe(II); 1 g/l CN4SG: 15,4 g/m²;

X=2000

Variant D: Ohne Fe(II); 6 g/l CN4SG: 12,8 g/m²;

X=2000

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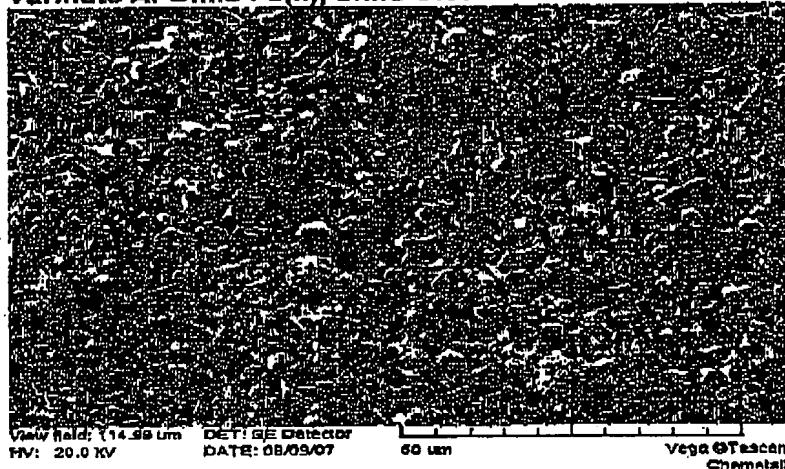
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P. 011

6120419; GBG4098; CN4 Patent

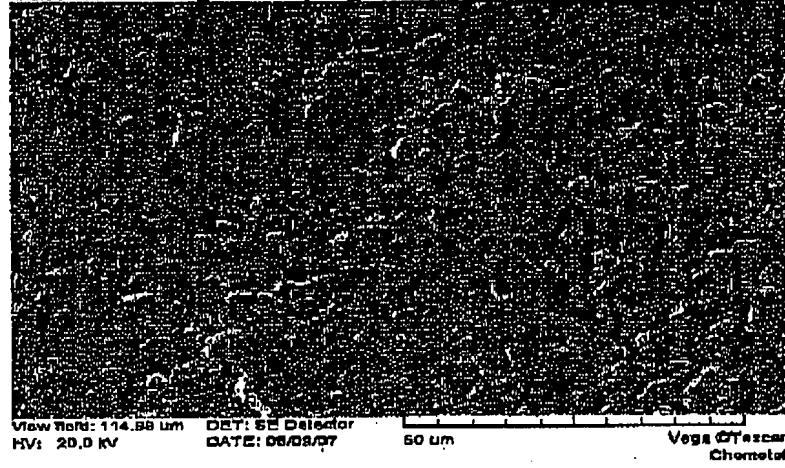
09.08.2007
SCDE

Varinate A: Ohne Fe(II), ohne CN4

SG: 12,7 g/m²

X=1000

Varianter C: 1 g/l Fe++; 1 g/l CN4

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CN4-Patent-1.doc

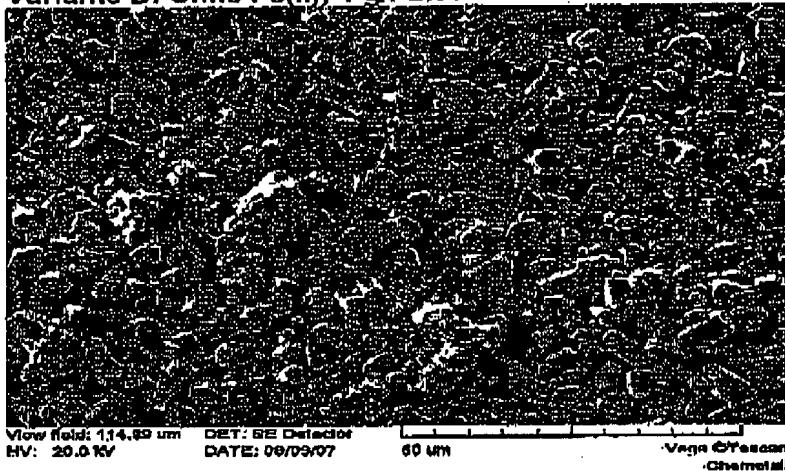
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P. 012

SG: 10,9 g/m²;

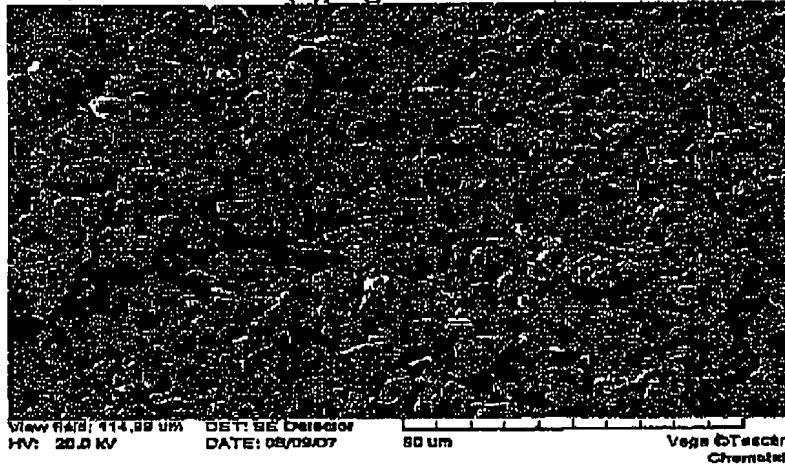
X=1000

Varilante B: Ohne Fe(II); 1 g/l CN4

View field: 114.89 µm DET: SE Detector
HV: 20.0 kV DATE: 08/09/07 80 µm Vega Gatan
Chemtall

SG: 15,4 g/m²;

X=1000

Varinate D: Ohne Fe(II); 6 g/l CN4

View field: 114.89 µm DET: SE Detector
HV: 20.0 kV DATE: 08/09/07 80 µm Vega Gatan
Chemtall

SG: 12,8 g/m²;

X=1000

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CN4-Patent-1.doc

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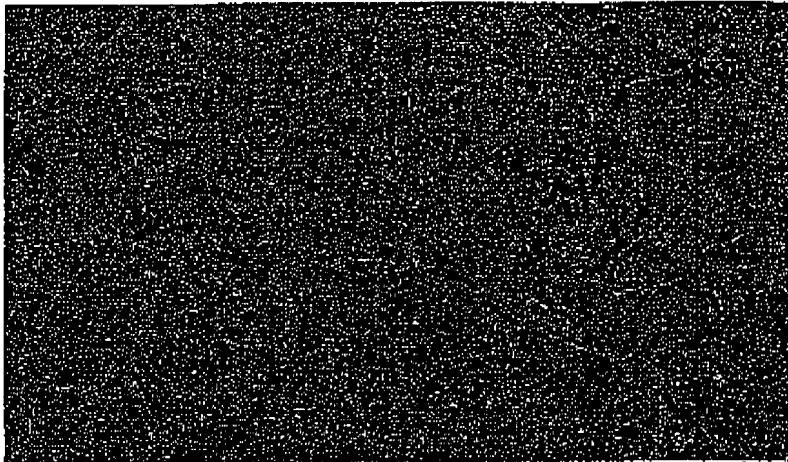
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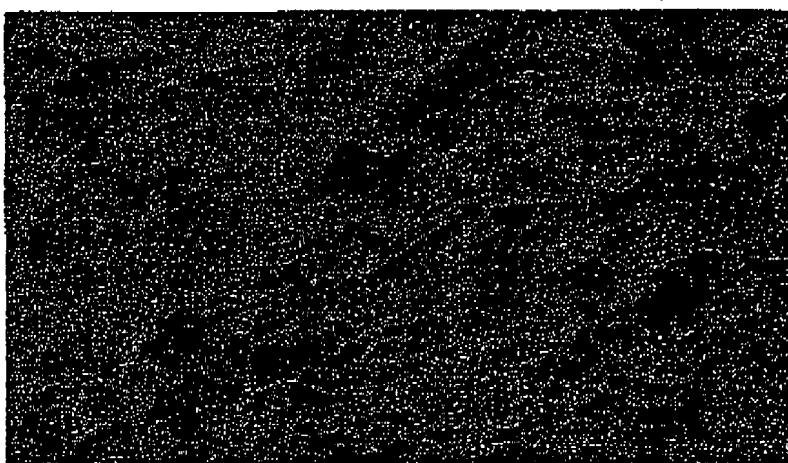
Enclosure II

Chemetall

US Patent 2,375,468;

Mangan-Phosphat; 201 g/l; GS 102; FS 17; SV 6,0 12.07.07 SCDE
RT 60min und 80°C 10min; KW aktiviert; Sidmar Stahlbleche

RT; 60min; BA: 1,6 g/m²; keine Schichtausbildung; X=500



80°C; 10'; BA: 19,9 g/m²; SG: 1,6 g/m²; keine geschl. Schichten; X=500

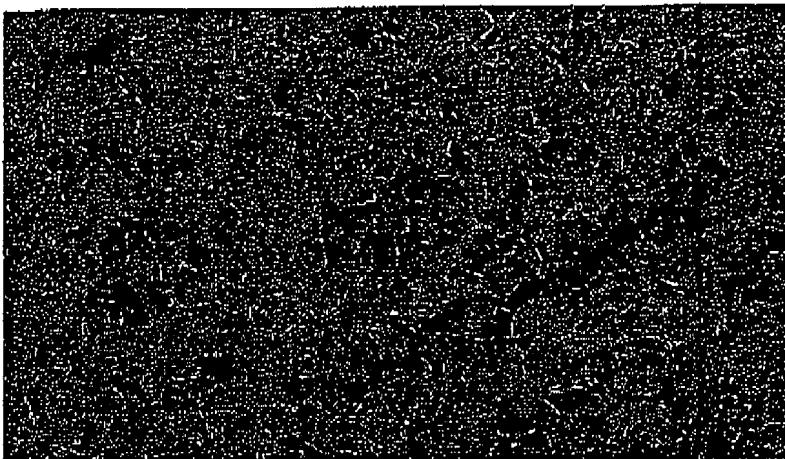


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Chemetall

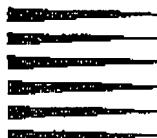
View Field: 229.38 μ m DET: SE Detector
HV: 20.0 kV DATE: 07/12/07 100 μ m
VAC: HVac Device: VEGA 5130MM
Vega @ Tescan
Chemetall

RT; 60min; BA: 17,8 g/m²; keine Schichtausbildung; X=500
0,3% CN4



View Field: 291.78 μ m DET: SE Detector
HV: 20.0 kV DATE: 07/12/07 100 μ m
VAC: HVac Device: VEGA 5130MM
Vega @ Tescan
Chemetall

80°C; 10'; BA: 17,6 g/m²; SG: 19,0 g/m²; keine geschl. Schichten; X=500
0,3 % CN4



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